Photochemistry of Ethyl 4-Substituted 2-Cyano-1,2-dihydroquinoline-1-carboxylates (Reissert Compounds): Syntheses of Cycloprop[*b*]indoles

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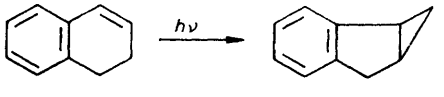
Irradiation of ethyl 4-substituted 2-cyano-1,2-dihydroquinoline-1-carboxylates (Reissert compounds) in ethanol gives ethyl 6b-substituted 1-cyano-1,1a,2,6b-tetrahydrocycloprop[*b*]indole-2-carboxylates. The stereochemistry of the products has been determined by n.m.r. spectroscopy.

THE photochemical valence isomerisation of 1,2-dihydronaphthalenes (1) to 1,1a,2,6b-cycloprop[*b*]indenes



(1) (2)

(2) is well established.[1] However, earlier attempts to duplicate this reaction in the heterocyclic series were unsuccessful. During studies on the photoisomerisation of ethyl 2-cyano-1,2-dihydroquinoline-1-carboxylates (Reissert compounds) to allenic compounds,[2] we have found that the introduction of a methyl group at the 4-position of the quinoline ring changes the reaction course: the product is ethyl *endo*-1-cyano-1,1a,2,6b-tetrahydro-6b-methylcycloprop[*b*]indole-2-carboxylate

[1] D. A. Seeley, *J. Amer. Chem. Soc.*, 1972, **94**, 4378; H. Heimgarter, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 3005, and references cited therein.

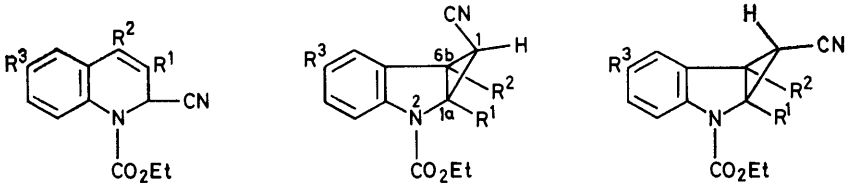
[2] M. Ikeda, S. Matsugashita, and Y. Tamura, *J.C.S. Perkin I*, 1976, 2587.

(4a).[3,*] We now report details of the photoisomerisation of quinoline Reissert compounds to cycloprop[*b*]indoles,† and the epimerisation of the products.

Synthesis.—All the Reissert compounds employed were synthesised as described by Popp and his co-workers.[4] As noted previously,[2] irradiation of the Reissert compound (3a) in ether with a 350 W high-pressure mercury lamp through Pyrex gave the cyclopropindole (4a) as a minor product, along with ethyl 2-cyanomethyl-3-methylindole-1-carboxylate (6) [which could arise by an intramolecular cyclisation of the allene (10)]. However, the same compound, on irradiation in ethanol produced exclusively compound (4a), in 61% yield. Similarly, irradiation of the Reissert compounds (3b and c) in ethanol gave the corresponding cyclopropindoles (4b and c) in 63 and 59% yields, respectively. In contrast, Reissert compounds derived from quinolines lacking a 4-substituent, such as quinoline itself or 3-methylquinoline, did not give cyclopropindoles under a variety of conditions.[2] These results prompted us to examine the effect of the other substituent(s) upon the photoisomerisation. However, 4-benzyl-, 4-ethoxycarbonyl-, and 4-chloro-quinolines did not give the corresponding Reissert compounds.

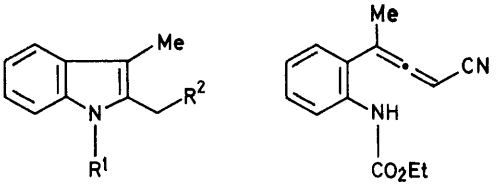
The 4-pentyl (3d) and 4-methoxymethyl (3e) derivatives isomerised to the corresponding cyclopropindoles (4d and e) in 66 and 35% yields, respectively. Irradiation of the 4-methoxy-derivative (3f) in ethanol gave a complex mixture from which (4f) was isolated in only 10% yield. Irradiation of the 4-phenyl derivative (3; $R^1 = R^3 = H$, $R^2 = Ph$) in ethanol again gave a complex mixture, which was not examined further.

In contrast to the reaction of the 4-methyl derivative (3a), which gave exclusively the *endo*-isomer (4a), irradiation of 3,4-dimethyl (3g) and 3,4-tetramethylene derivatives (3h) in ethanol afforded mixtures of *endo*- and *exo*-isomers, (4g and h) and (5g and h), respectively. Since these compounds were stable under the conditions employed, these are considered to be primary products.



(3) (4) (5)

a; $R^1 = R^3 = H$, $R^2 = Me$
b; $R^1 = H$, $R^2 = R^3 = Me$
c; $R^1 = H$, $R^2 = Me$, $R^3 = OMe$
d; $R^1 = R^3 = H$, $R^2 = [CH_2]_4 \cdot CH_3$
e; $R^1 = R^3 = H$, $R^2 = CH_2 \cdot OMe$
f; $R^1 = R^3 = H$, $R^2 = OMe$
g; $R^1 = R^2 = Me$, $R^3 = H$
h; $R^1 R^2 = [CH_2]_4$, $R^3 = H$



(6) $R^1 = CO_2Et$, $R^2 = CN$
(7) $R^1 = R^2 = CO_2Et$
(8) $R^1 = H$, $R^2 = CO_2Et$
(9) $R^1 = CO_2Et$, $R^2 = CONH_2$

(10)

The structures of the cyclopropindoles were established by a combination of spectroscopic and chemical evidence. For example, compound (4a) has the parent ion peak at *m/e* 242 in its mass spectrum, indicating that it is isomeric with (3a). The u.v. spectrum of (4a) ($\lambda_{max.}$ 245, 281, and 289 nm) is typical of 1-acylindolines.[5] Its i.r. spectrum reveals the presence of a carbonyl group (1 710 cm^{-1}) and a cyano group (2 240 cm^{-1}), and its n.m.r. spectrum shows a doublet due to H-1 (*J* 6 Hz) at δ 1.75, a quartet ascribable to $CO_2 \cdot CH_2 \cdot CH_3$ (*J* 7 Hz) overlapped with a doublet due to H-1a (*J* 6 Hz) at δ 4.40, a singlet due to the 6b-methyl group at δ 1.67, a triplet (*J* 7 Hz, $CO \cdot CH_2 \cdot CH_3$) at δ 1.41, a broad signal due to H-3 at δ *ca.* 7.5—8.0, and an aromatic three-proton multiplet between δ 7.0 and 7.4.

Chemical confirmation for this structure was obtained

* After our preliminary communication [3] had appeared, Padwa and his co-workers reported the analogous photoisomerisation of isochromens to indene oxides (A. Padwa, A. Au, G. A. Lee, and W. Owens, *J. Org. Chem.*, 1975, **40**, 1142).

† The only reported examples of this class of compounds are ethyl 2-benzoyl-1,1a,2,6b-tetrahydrocycloprop[*b*]indole-1-carboxylates, synthesised by the reaction of 1-benzoylindoles with ethyl diazoacetate in low yields (W. J. Welstead, jun., H. F. Stauffer, jun., and L. F. Sancilio, *J. Medicin. Chem.*, 1974, **17**, 544).

[3] M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi, and Y. Tamura, *J.C.S. Chem. Comm.*, 1974, 433.
[4] F. D. Popp, L. E. Katz, C. W. Klinowski, and J. M. Wefer, *J. Org. Chem.*, 1968, **33**, 4447.
[5] B. Gilbert, 'The Alkaloids,' ed. H. F. Manske, Academic Press, New York, 1965, vol. 8, p. 335.

by cyclopropane ring opening of (4a) with acid to give 2-substituted indoles. Thus, when (4a) was refluxed in concentrated hydrochloric acid, the 2-cyanomethyl-3-methylindole (6) [2] was obtained in 42% yield. Treatment of (4a) with ethanolic hydrogen chloride at −5 °C gave ethyl 1-ethoxycarbonyl-3-methylindol-2-ylacetate (7) in 90% yield, which, upon treatment with potassium carbonate in methanol was readily hydrolysed to ethyl 3-methylindol-2-ylacetate (8).[6] Heating (4a) in polyphosphoric acid at 60—70 °C gave 1-ethoxycarbonyl-3-methylindol-2-ylacetamide (9) in 93% yield.

The stereochemistry of the cyano-group in compounds (4) was assigned on the basis of epimerisation studies described later.

Previously we suggested [3] that the formation of the cyclopropindole can be interpreted in terms of an intermediate azahexatriene, by analogy with the photoisomerisation of 1,2-dihydronaphthalenes [(1) ⟶ (2)]. A preliminary mechanistic study, however, showed that the reaction [(3) ⟶ (4)] is mechanistically different from that of the carbocyclic system and that an azahexatriene is not an intermediate. The details will be reported separately.

Epimerisation.—In initial experiments on the photoisomerisation of the Reissert compounds (3), it was noted that the reaction proceeds stereospecifically to give exclusively the *endo*-isomer (4). To obtain a firm basis for the stereochemistry of the cyano-group, the *exo*-isomers were required. Epimerisation was accomplished by three methods: (i) refluxing in decalin, (ii) acetone-sensitised photolysis, and (iii) treatment with boron trifluoride–ether in refluxing benzene. From the *endo*-isomer (4a) an equilibrium mixture containing almost equal amounts of the isomers (4a) and (5a) was obtained, irrespective of the method used.* The isomers were readily separated by preparative t.l.c. The *exo*-isomers (5b—f) were obtained similarly.

N.m.r. spectra for cycloprop[*b*]indoles (δ values; solvent $CDCl_3$)

	H-1	H-1a(R^1)	R^2	$J_{1.1a}$Hz	$CO_2{\cdot}CH_2{\cdot}CH_3$	$CO_2{\cdot}CH_2{\cdot}CH_3$	Aromatic H	Other
(4a)	1.75 (d)	4.40 (d)	1.67 (3 H, s)	6	4.40 (q)	1.41 (t)	7.5—8.0 (1 H), 7.0—7.4 (3 H, m)	
(5a)	1.08 (d)	4.47 (d)	1.81 (3 H, s)	2	4.38 (q)	1.41 (t)	7.88 (1 H, d), 7.0—7.4 (3 H, m)	
(4b)	1.72 (d)	4.37 (d)	1.62 (3 H, s)	6	4.37 (q)	1.40 (t)	7.3—7.7br (1 H), 7.12br (1 H, s), 7.09br (1 H, d)	2.35 (3 H, s, 5-CH_3)
(5b)	1.02 (d)	4.40 (d)	1.88 (3 H, s)	2	4.34 (q)	1.49 (t)	7.60br (1 H, d), 7.10br (1 H, s), 7.00br (1 H, d)	2.31 (3 H, s, 5-CH_3)
(4c)	1.72 (d)	4.38 (d)	1.64 (3 H, s)	6	4.38 (q)	1.40 (t)	7.5—7.9br (1 H), 6.87br (1 H, s), 6.81 (1 H, dd)	3.80 (3 H, s, OCH_3)
(5c)	1.10 (d)	4.45 (d)	1.80 (3 H, s)	2	4.32 (q)	1.40 (t)	7.63br (1 H, d), 6.89 (1 H, d), 6.79 (1 H, dd)	3.82 (3 H, s, OCH_3)
(4d)	1.77 (d)	4.40 (d)	0.8—2.5 (11 H, m)	6	4.38 (q)	1.40 (t)	7.7fbr (1 H, d), 7.0—7.4 (3 H, m)	
(5d)	1.08 (d)	4.43 (d)	0.8—2.6 (11 H, m)	2	4.37 (q)	1.40 (t)	7.74br (1 H, d), 6.9—7.4 (3 H, m)	
(4e)	2.08 (d)	4.60 (d)	3.89 (2 H, ABq, *J* 10 Hz, $CH_2{\cdot}OMe$)	6	4.36 (q)	1.39 (t)	7.5—7.9br (1 H), 6.95—7.35 (3 H, m)	3.36 (3 H, s, OCH_3)
(5e)	1.20 (d)	4.61 (d)	4.00br (2 H, s)	2	4.38 (q)	1.40 (t)	7.76br (1 H, d), 6.9—7.6 (3 H, m)	3.48 (3 H, s, OCH_3)
(4f)	2.31 (d)	4.67 (d)	3.40 (3 H, s, OCH_3)	7	4.40 (q)	1.42 (t)	7.66br (1 H, d), 7.0—7.7 (3 H, m)	
(5f)	1.32 (d)	4.72 (d)	3.52 (3 H, s, OCH_3)	2	4.38 (q)	1.43 (t)	7.80br (1 H, d), 7.0—7.6 (3 H, m)	
(4g)	1.75 (s)	1.75 (3 H, s)	1.58 (3 H, s)		4.39 (q)	1.41 (t)	7.75br (1 H, d), 6.9—7.5 (3 H, m)	
(5g)	1.30 (s)	1.85 (3 H, s)	1.79 (3 H, s)		4.38 (q)	1.41 (t)	7.73br (1 H, d), 7.0—7.4 (3 H, m)	
(4h)	1.81 (s)	2.0—2.6br (4 H), 1.1—1.6br (4 H)			4.39 (q)	1.40 (t)	7.79br (1 H, d), 6.9—7.4 (3 H, m)	
(5h)	1.29 (s)	2.0—2.7br (4 H), 1.2—1.7br (4 H)			4.38 (q)	1.41 (t)	7.75br (1 H, d), 6.9—7.5 (3 H, m)	

The stereochemistry of the cyano-group was ascertained from n.m.r. spectra (Table). (i) In the *exo*-isomers the H-1 signal occurs 0.6—0.7 p.p.m. to higher field than that of the H-1 in the *endo*-isomers. Models reveal that H-1 in the *exo*-isomers lies in the shielding cone of the benzene ring. (ii) The observed couplings (6—7 Hz) between H-1 and H-1a in the *endo*-isomers and the smaller coupling (2 Hz) in *exo*-isomers agree well with reported values for the vicinal couplings in *endo*- (11) (7.5 Hz) and *exo*-isomers (12) (3.1 Hz) of 7-cyanocycloprop[*a*]acenaphthylenes,[7] respectively.

Recently the mechanism of the photo-induced epimerisation of bicyclo[3.1.0]hexene derivatives has been investigated.[8,9] For example, Garin and his co-workers,[8]

* Similar results were obtained from the *exo*-isomer (5a).

[6] H. H. Stroh and H. Beitz, *Annalen*, 1966, **700**, 78.

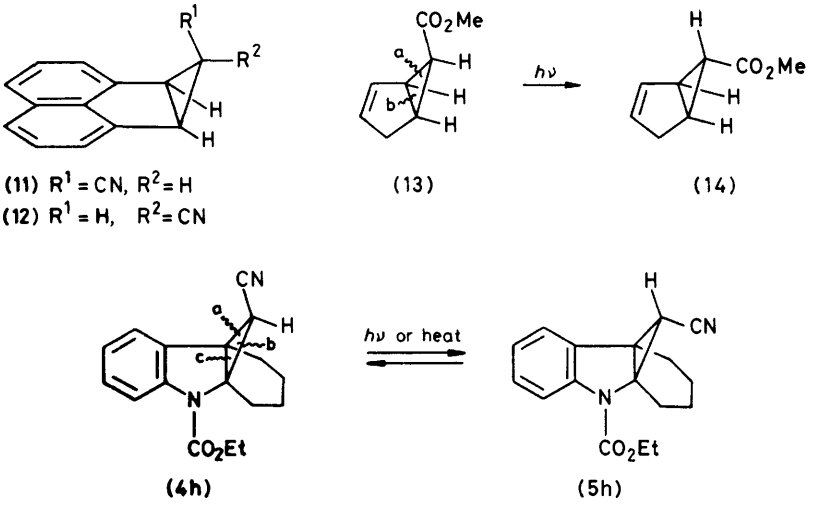
[7] V. Rautenstrauch and F. Wingler, *Tetrahedron Letters*, 1965, 4703.

[8] D. L. Gain and D. J. Cooke, *J.C.S. Chem. Comm.*, 1972, 33.

[9] S. S. Hixson and J. Borovsky, *J. Amer. Chem. Soc.*, 1976, **98**, 2840.

using optically active methyl bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxylate (**13**), demonstrated that epimerisation to (**14**) proceeds *via* cleavage of the external bond (a) rather than the internal bond (b). It seemed of interest to discover the effect of a heteroatom on this epimerisation reaction.

To discover whether epimerisation of the cycloprop[*b*]-indoles takes place *via* external bond cleavage [(a) or (b)] the photochemistry of (4h) and (5h) was examined, in which epimerisation *via* the alternative internal bond cleavage (c) would be inhibited by the presence of the



cyclohexane ring. Irradiation of either (4h) or (5h) in acetone for 8 h gave a *ca.* 1 : 1 equilibrium mixture of isomers. The epimerisation also took place under thermal conditions. Consequently a mechanism involving external bond cleavage [(a) or (b)] is suggested.

EXPERIMENTAL

N.m.r. spectra were determined with a Hitachi R-22 spectrometer (90 MHz; tetramethylsilane as internal standard). I.r. spectra were recorded with a Hitachi EPI-G2 spectrometer and u.v. spectra with a Hitachi 124 spectrometer. Low and high resolution mass spectra were obtained with a Hitachi RMU-6D and a JEOL-JMS-01SG instrument with a direct inlet system, operating at 70 and 75 eV, respectively. Irradiations were carried out with an Eikosha 350 W high-pressure mercury lamp. Merck PF_{254} alumina was used for p.l.c.

Materials.—4-Methylquinoline was obtained commercially. 4,6-Dimethylquinoline,[10] 6-methoxy-4-methylquinoline,[10] 4-methoxyquinoline,[11] 4-phenylquinoline,[12] 3,4-dimethylquinoline,[13] and 7,8,9,10-tetrahydrophenanthridine [14] were synthesised as described in the literature.

4-Methoxymethylquinoline.—A solution of quinolin-4-ylmethanol [15] (2.7 g) and thionyl chloride (3 ml) in chloroform (10 ml) was kept at room temperature for 1 h, then concentrated. The residue was diluted with water, made alkaline with 10% sodium hydroxide, and extracted with ether. The extract was dried ($MgSO_4$) and concentrated to give 4-chloromethylquinoline (2.2 g), m.p. 55—56° [from light petroleum (b.p. 30—60 °C)] (lit.,[16] 56—57°). A solution of 4-chloromethylquinoline (1.6 g) and sodium methoxide (1.6 g) in dry methanol (30 ml) was refluxed for 2 h, then evaporated. The residue was diluted with water and extracted with ether. The extract was dried ($MgSO_4$) and concentrated. The oily residue was distilled to give 4-methoxymethylquinoline (948 mg), b.p. 142—145° at 6 mmHg. The *picrate* had m.p. 195° (from methanol) (Found: C, 50.4; H, 3.5; N, 13.9. $C_{17}H_{14}N_4O_8$ requires C, 50.75; H, 3.5; N, 13.9%).

4-Pentylquinoline.—By application of the procedure of Kaiser,[17] 4-pentylquinoline (480 mg) was prepared from 4-methylquinoline (2 g) and n-butyl bromide (1.9 g); b.p. 155—158° at 9 mmHg. The *picrate* had m.p. 161—162° (from ethanol) (Found: C, 55.7; H, 4.65; N, 13.3. $C_{20}H_{20}N_4O_7$ requires C, 56.1; H, 4.7; N, 13.1%).

Reissert Compounds (3b—h).—The Reissert compounds (3) were prepared from the corresponding quinolines according to the method described by Popp and his co-workers.[4] *Ethyl 2-cyano-1,2-dihydro-4,6-dimethylquinoline-1-carboxylate* (3b) (44%) had m.p. 129—130° (from ethanol) (Found: C, 70.3; H, 6.3; N, 10.9. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%); the *6-methoxy-4-methyl-derivative* (3c) (39%) had m.p. 120° (from ethanol) (Found: C, 66.1; H, 6.0; N, 10.2. $C_{25}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); the *4-pentyl derivative* (3d) (48%) was an oil (Found: *m/e*, 298.1679. $C_{18}H_{22}N_2O_2$ requires *M*, 298.1681); the *4-methoxymethyl derivative* (3e) (34%) had m.p. 90—91° [from light petroleum (b.p. 60—80 °C)] (Found: C, 66.1; H, 5.8; N, 10.2. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); the *4-methoxy-derivative* (3f) (47%) had m.p. 127—128° (from ethanol) (Found: C, 65.3; H, 5.4; N, 10.75. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5;

[10] K. N. Campbell and I. J. Schaffner, *J. Amer. Chem. Soc.*, 1945, **67**, 86.
[11] J. R. Keneford, J. S. Morley, J. C. E. Simpson, and P. H. Wright, *J. Chem. Soc.*, 1950, 1104.
[12] C. F. Koelsch and A. F. Steinhauer, *J. Org. Chem.*, 1953, **18**, 1516.
[13] S. G. P. Plant and R. J. Rosser, *J. Chem. Soc.*, 1930, 2444.
[14] B. L. Hollingsworth and V. Petrow, *J. Chem. Soc.*, 1948, 1537.
[15] S. F. MacDonald, *J. Amer. Chem. Soc.*, 1947, **69**, 1219.
[16] H. Tanida, *J. Pharm. Soc. Japan*, 1958, **78**, 611.
[17] E. M. Kaiser and J. D. Petty, *J. Org. Chem.*, 1976, **41**, 716.

N, 10.85%); the *4-phenyl derivative* (3; $R^1 = R^3 = H$, $R^2 = Ph$) (32%) had m.p. 129—130° (from ethanol) (Found: C, 75.0; H, 5.2; N, 9.2. $C_{19}H_{16}N_2O_2$ requires C, 75.0; H, 5.3; N, 9.2%); the *3,4-dimethyl derivative* (3g) (47%) had m.p. 123—124° (from methanol) (Found: C, 70.4; H, 6.3; N, 10.9. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%); *ethyl 6-cyano-5,6,7,8,9,10-hexahydrophenanthridine-5-carboxylate* (3h) (20%) had m.p. 143—144° (from ethanol) (Found: C, 72.25; H, 6.4; N, 9.9. $C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.4; N, 9.9%).

Irradiation of The Reissert Compound (3a).—(*a*) A solution of compound (3a) (5 g) in ethanol (350 ml) in an immersion apparatus (Pyrex filter) was irradiated at 2 °C until the starting material had disappeared (4 h) (t.l.c.). Evaporation afforded a solid which was recrystallised from light petroleum (b.p. 60—80 °C) to give *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-6b-*methylcycloprop*[b]*indole*-2-*carboxylate* (4a) (2.3 g, 46%), m.p. 104—105° (Found: C, 69.4; H, 5.9; N, 11.3. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N, 11.6%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 245, 281, and 289 nm (log ε 4.02, 3.31, and 3.27); *m/e* 242 (M^+).

(*b*) Irradiation of a solution of (3a) (300 mg) in ethanol (40 ml) in a Pyrex tube for 4 h gave (4a) (183 mg, 61%).

Irradiation of Compound (3b).—A solution of (3b) (144 mg) in ethanol (20 ml) was irradiated in a Pyrex tube for 5 h and concentrated. The residue was purified by preparative t.l.c. (benzene as solvent) to give *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-5,6b-*dimethylcycloprop*[b]*indole*-2-*carboxylate* (4b) (91 mg, 63%) as an oil; $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 212, 241, 280, and 288 nm (log ε 4.69, 4.30, 3.60, and 3.56) (Found: *m/e*, 256.1184. $C_{15}H_{16}N_2O_2$ requires *M*, 256.1211).

Irradiation of Compound (3c).—A solution of (3c) (70 mg) in ethanol (10 ml) was irradiated in a Pyrex tube for 5 h and concentrated. The residue was recrystallised from light petroleum (b.p. 60—80 °C) to give *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-5-*methoxy*-6b-*methylcycloprop*[b]*indole*-2-*carboxylate* (4c) (36 mg, 59%), m.p. 124—125° (Found: C, 66.05; H, 5.9; N, 10.3. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ (KCl) 2 240 and 1 715 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 248 and 296 nm (log ε 3.07 and 2.49); *m/e* 272 (M^+).

Irradiation of Compound (3d).—A solution of (3d) (150 mg) in ethanol (20 ml) was irradiated in a Pyrex tube for 10 h and concentrated. The residual oil was purified by preparative t.l.c. (benzene as solvent) to give *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-6b-*pentylcycloprop*[b]*indole*-2-*carboxylate* (4d) (99 mg, 66%) as an oil; $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 236, 273, and 282 nm (log ε 4.10, 3.27, and 3.22); (Found: *m/e*, 298.1681. $C_{18}H_{22}N_2O_2$ requires *M*, 298.1681).

Irradiation of Compound (3e).—A solution of (3e) (108 mg) in ethanol (14 ml) was irradiated in a Pyrex tube for 8 h and concentrated. The residual oil was purified by preparative t.l.c. (benzene as solvent) to give *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-6b-*methoxymethylcycloprop*[b]*indole*-2-*carboxylate* (4e) (38 mg, 35%) as an oil; $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 216, 245, 282, and 291 nm (log ε 4.31, 4.07, 3.30, and 3.26) (Found: *m/e*, 272.1129. $C_{15}H_{16}N_2O_3$ requires *M*, 272.1160).

Irradiation of Compound (3f).—A solution of (3f) (150 mg) in ethanol (20 ml) was irradiated in a Pyrex tube for 9 h and concentrated to give a complex mixture, from which *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-6b-*methoxycycloprop*[b]*indole*-2-*carboxylate* (4f) was isolated in 10% yield as an oil by preparative t.l.c. [ether–light petroleum (b.p. 30—60 °C) (1 : 1)]; $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 210, 243, 287, and 294 nm (log ε 4.59, 4.00, 3.31, and 3.14) (Found: *m/e*, 258.1002. $C_{14}H_{14}N_2O_3$ requires *M*, 258.1004).

Irradiation of Compound (3g).—(*a*) A solution of (3g) (50 mg) in ethanol (7 ml) was irradiated in a Pyrex tube for 5 h and concentrated to give a mixture of two products, which were separated by preparative t.l.c. [ether–light petroleum (b.p. 30—60 °C) (1 : 4)]. The major product crystallised from light petroleum (b.p. 60—80 °C) to give needles of *ethyl* endo-1-*cyano*-1,1a,2,6b-*tetrahydro*-1a,6b-*dimethylcycloprop*[b]*indole*-2-*carboxylate* (4g) (39 mg, 79%), m.p. 95—96° (Found: C, 70.35; H, 6.3; N, 11.0. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 216, 247, 282, and 292 nm (log ε 4.42, 4.02, 3.30, and 3.25); *m/e* 256 (M^+).

The minor product crystallised from light petroleum (b.p. 60—80 °C) to give needles (10 mg, 20%) of the exo-*isomer* (5g), m.p. 113—114° (Found: C, 70.5; H, 6.3; N, 10.7%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 217, 248, 284, and 292 (log ε 4.48, 4.05, 3.48, and 3.44); *m/e* 256 (M^+).

(*b*) Irradiation of a solution of (3g) (50 mg) in ether (7 ml) in a Pyrex tube for 5 h gave (4g) and (5g) in 58 and 40% yields, respectively.

Irradiation of Compound (3h).—(*a*) A solution of (3h) (150 mg) in ethanol (20 ml) was irradiated in a Pyrex tube for 5 h and concentrated to give a mixture of two products, which were separated by preparative t.l.c. (benzene as solvent). The major product crystallised from light petroleum (b.p. 60—80 °C) to give needles of *ethyl* endo-10-*cyano*-2,3,4,4a,9,9a-*hexahydro*-4a,9a-*methano*-1H-*carbazole*-9-*carboxylate* (4h) (70 mg, 47%), m.p. 93—94° (Found: C, 72.1; H, 6.4; N, 9.7. $C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.4; N, 9.9%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 217, 247, 283, and 292 (log ε 4.39, 4.05, 3.33, and 3.04); *m/e* 282 (M^+).

The minor product crystallised from light petroleum (b.p. 60—80 °C) to give needles of the exo-*isomer* (5h) (35 mg, 23%), m.p. 144—145° (Found: C, 72.25; H, 6.4; N, 9.9%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 216, 249, 284, and 292 (log ε 4.45, 4.14, 3.63, and 3.58); *m/e* 282 (M^+).

(*b*) Irradiation of a solution of (3h) (50 mg) in ether (7 ml) in a Pyrex tube for 5 h gave (4h) and (5h) in 30 and 38% yields, respectively.

Ethyl 2-Cyanomethyl-3-methylindole-1-carboxylate (6).—Compound (4a) (108 mg) in concentrated hydrochloric acid was refluxed for 2.5 h. After cooling, the mixture was extracted with chloroform. The extract was washed with saturated aqueous sodium carbonate, dried ($MgSO_4$), and concentrated. The residue was recrystallised from light petroleum (b.p. 30—60 °C) to give compound (6) (46 mg, 42%), m.p. 89—90°, identical with an authentic sample.[2]

Ethyl 3-Methylindol-2-ylacetate (8).—A solution of compound (4a) (73 mg) in absolute ethanol (5 ml) was saturated with dry hydrogen chloride at −5 °C. The mixture was set aside at room temperature overnight and concentrated to give crude ethyl 1-ethoxycarbonyl-3-methylindol-2-ylacetate (7) (90 mg), m.p. 152—153°; $\nu_{max.}$ (KCl) 1 730 cm^{-1}; *m/e* 289 (M^+), which was hydrolysed without further purification. A suspension of compound (7) (97 mg) and potassium carbonate (100 mg) in methanol (5 ml) was stirred at room temperature for 5 h. The potassium carbonate was filtered off, the filtrate concentrated, and the residual solid purified by preparative t.l.c. (chloroform as solvent) and

recrystallisation from aqueous methanol to give the product (8) (40 mg, 52%); m.p. 99—100.5° (lit.,[6] 98—100°).

1-*Ethoxycarbonyl*-3-*methylindol*-2-*ylacetamide* (9).—A mixture of compound (4a) (152 mg) and polyphosphoric acid (800 mg) was heated at 60—70 °C with occasional stirring for 2 h, then poured into ice–water. The precipitated white solid was collected and recrystallised from benzene–light petroleum (b.p. 80—100 °C) to give the *amide* (9) (153 mg, 93%), m.p. 190—191° (Found: C, 64.5; H, 6.3; N, 10.7. $C_{14}H_{16}N_2O_3$ requires C, 64.6; H, 6.2; N, 10.8%); $\nu_{max.}$ (KCl) 3 380, 3 200, 1 725, and 1 660 cm^{-1}; δ ($CDCl_3$) 8.15—8.05 (1 H, m, H-7), 7.2—7.6 (3 H, m, H-4, -5, and -6), 5.4—5.9br (2 H, NH_2), 4.49 (2 H, q, *J* 7 Hz, $CO_2{\cdot}CH_2{\cdot}CH_3$), 3.96 (2 H, s, CH_2), 2.27 (3 H, s, CH_3), and 1.47 (3 H, t, *J* 7 Hz, $CO_2{\cdot}CH_2{\cdot}CH_3$); $\lambda_{max.}$ (EtOH) 228, 263, 283, and 294 nm (log ε 4.19, 3.94, 3.55, and 3.42); *m/e* 260 (M^+).

Thermal Epimerisation.—A solution of compound (4a) (500 mg) in decalin (20 ml) was refluxed; the reaction was followed by n.m.r. spectroscopy. After 20 h the solvent was evaporated off *in vacuo* to give an equilibrium mixture of (4a) and (5a) in the ratio *ca.* 1 : 1 (by n.m.r.). The isomers were separated by preparative t.l.c. [benzene–n-hexane (1 : 1) as solvent] to give (4a) (200 mg) and (5a) (165 mg). The exo-*isomer* (5a) had m.p. 98—99° [from light petroleum (b.p. 60—80 °C)] (Found: C, 69.6; H, 5.8; N, 11.5. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N, 11.6%); $\nu_{max.}$ (KCl) 2 210 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 212, 245, 280, and 289 nm (log ε 4.62, 4.18, 3.47, and 3.42); *m/e* 242 (M^+). Similar treatment of (5a) (15 mg) gave an equilibrium mixture of (4a) and (5a) (*ca.* 1 : 1) after 15 h.

By this procedure, (4h) (25 mg) gave an equilibrium mixture of (4h) and (5h) (*ca.* 1 : 1), and (5h) (25 mg) gave an equilibrium mixture of (4h) and (5h) (*ca.* 1 : 1) after 15 h.

Acetone-sensitised Photoepimerisation.—A solution of compound (4a) (75 mg) in acetone (10 ml) was irradiated in a Pyrex tube; the reaction was followed by n.m.r. spectroscopy. After 8 h, the solvent was removed to give an equilibrium mixture of (4a) and (5a) in the ratio *ca.* 1 : 1 (by n.m.r.). Similarly (5a) gave an equilibrium mixture of (4a) and (5a) in the ratio *ca.* 1 : 1 after 8 h. Irradiation of (4h) or (5h) under similar conditions gave an equilibrium mixture of (4h) and (5h) in the ratio *ca.* 1 : 1.

In order to obtain the *exo*-isomers (5b—f), the corresponding *endo*-isomers (4b—f) were irradiated in acetone for 5.5 h and the resulting mixture of *endo*- and *exo*-isomers was separated by preparative t.l.c. [ether–light petroleum (1 : 1) as solvent]. Compound (4b) (94 mg) gave a mixture of (4b) (30 mg, 32%) and the *exo*-isomer (5b) (22 mg, 23%); *compound* (5b) had m.p. 127—128° [from light petroleum (b.p. 60—80 °C)] (Found: C, 70.3; H, 6.3; N, 10.9. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 240, 278, and 288 nm (log ε 4.16, 3.35, and 3.33); (4c) (85 mg) gave a mixture of (4c) (48 mg, 57%) and the *exo*-isomer (5c) (27 mg, 32%); *compound* (5c) had m.p. 119—120° [from light petroleum (b.p. 60—80 °C)](Found: C, 66.1; H, 6.0; N, 10.2. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 210, 250, and 299 nm (log ε 3.54, 3.19, and 2.60); *m/e* 272 (M^+); (4d) (99 mg) gave a mixture of (4d) (56 mg, 57%) and the *exo*-isomer (5d) (41 mg, 41%); *compound* (5d) had m.p. 81—82° [from light petroleum (b.p. 60—80 °C)] (Found: C, 72.6; H, 7.5; N, 9.4. $C_{18}H_{22}N_2O_2$ requires C, 72.45; H, 7.4; N, 9.4%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 238, 274, and 282 nm (log ε 4.13, 3.45, and 3.42); *m/e* 298 (M^+); (4e) (38 mg) gave a mixture of (4e) (11 mg, 30%) and the *exo*-isomer (5e) (10 mg, 26%); *compound* (5e) had m.p. 105° [from light petroleum (b.p. 60—80 °C)] (Found: C, 65.9; H, 5.8; N, 10.35. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 216, 248, 284, and 292 nm (log ε 4.54, 4.17, 3.49, and 3.47); *m/e* 272 (M^+); (4f) (85 mg) gave a mixture of (4f) (48 mg, 57%) and the *exo*-isomer (5f) (27 mg, 32%); *compound* (5f) had m.p. 124—125° [from light petroleum (b.p. 60—80 °C)] (Found: C, 65.4; H, 5.4; N, 10.7. $C_{15}H_{16}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.85%); $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 710 cm^{-1}; $\lambda_{max.}$ (EtOH) 216, 246, 284, and 292 (log ε 4.48, 4.17, 3.53, and 3.50); *m/e* 258 (M^+).

Epimerisation with Boron Trifluoride–Ether.—A solution of compound (4a) (310 mg) and boron trifluoride–ether (43 mg) in dry benzene (5 ml) was refluxed for 2.5 h. The solvent was evaporated off and the residue submitted to preparative t.l.c. [benzene–n-hexane (1 : 1) as solvent] to give compounds (4a) (105 mg, 34%) and (5a) (128 mg, 42%) (*ca.* 1 : 1.2 by n.m.r.).

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